J. Chem. Thermodynamics 105 (2017) 50–57

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Relationships between fusion, solution, vaporization and sublimation enthalpies of substituted phenols

Mikhail I. Yagofarov, Ruslan N. Nagrimanov, Boris N. Solomonov *

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya Str. 18, 420008 Kazan, Russia

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form 17 September 2016
Accepted 24 September 2016
Available online 26 September 2016

Keywords:
Enthalpy of sublimation
Enthapy of vaporization
Enthalpy of fusion
Enthalpy of solution
Phenols

ABSTRACT

In this work a method for determination of sublimation and vaporization enthalpies of substituted phenols was developed. This method is a modification of solution calorimetry approach. Modification is based on the novel relations, which bind solution, vaporization and sublimation enthalpies at 298.15 K and fusion enthalpy at the melting temperature. According to novel relations the equations for calculating sublimation and vaporization enthalpies at 298.15 K were offered. Calculated values of sublimation and vaporization enthalpies of phenol derivatives containing alkyls, halogens, $-OCH_3$, $-NO_2$, $-COCH_3$, $-COOCH_3$ groups, and dihydroxybenzenes were compared with literature data (298.15 K) obtained by conventional methods. In most of the cases divergence does not exceed 2–3%.

1. Introduction

Being involved in large-scale production, phenols are dangerous ecotoxicants and may constitute a menace to the environment. Various data, including thermodynamics of fusion and evaporation, are necessary to estimate this threat.

Many different methods of determination of phase transition enthalpies exist. However, these methods demonstrate good reproducibility in case of highly volatile and volatile compounds. Essential discrepancies observed among the data typically appear when tested compounds are low volatile and thermally unstable.

We develop new approaches [1–7] for determination of fusion, vaporization and sublimation enthalpies at 298.15 K. These approaches do not have the difficulties mentioned above.

Our method [1] bases on the usage of solution calorimetry at 298.15 K as an experimental tool. Another value important for determination of evaporation enthalpy is the enthalpy of solvation. We elaborated various empirical methods of calculation of this value [1,2]. The experimental enthalpies of solution of a wide class of aromatic and heteroaromatic substances in different solvents together with calculated solvation enthalpies allowed determining the enthalpies of sublimation and vaporization of more than 100 compounds [1–4].

It was found in the work [5] that for a lot of aromatic compounds solution enthalpies in benzene at 298.15 K are approximately equal to experimentally measured enthalpies of fusion at melting temperature. A new approach for determination of sublimation enthalpy at 298.15 K through the fusion enthalpy at the melting temperature T_m and calculated solvation enthalpy was designed and was also successively applied for calculation of sublimation enthalpies of more than 100 compounds [5–7].

Systematic equality of experimental fusion enthalpy and solution enthalpy at 298.15 K is possible only if two conditions are met. Firstly, temperature weakly affects the magnitude of fusion enthalpy. Secondly, the enthalpy of solution in benzene at 298.15 K of compound in hypothetical liquid state is approximately equal to zero. It should be also noticed that polymorphic transitions between 298.15 K and fusion temperature must be absent for implementation of mentioned equality, otherwise a sum of their enthalpies should be added. However, our approach for determination of sublimation enthalpy may be also applied to the case of non-zero solution effect. It relates to the compounds capable of self-association due to hydrogen bonding.

In the present work we show that relationships between fusion, solution and sublimation enthalpies of substituted phenols are also observed.

2. Experimental part

2.1. Materials

Substituted phenols were of commercial origin. 3 and 4-Nitrophenol were purified by recrystallization from ethanol.

* Corresponding author.
E-mail address: boris.solomonov@kpfu.ru (B.N. Solomonov).

http://dx.doi.org/10.1016/j.jct.2016.09.029
0021-9614/